

HYDROGEN SULFIDE: AN EFFECTIVE REAGENT FOR REDUCING THE ELEMENTAL MERCURY CONTENT OF LIQUID HYDROCARBONS.

by

Costi A. Audeh

Central Research Laboratory
Mobil Research and Development Corporation
P. O. Box 1025
Princeton, NJ 08543-1025

Abstract

Elemental mercury has been identified in various crude oils and in condensates associated with the production of natural gas. When these liquid hydrocarbons are distilled or further processed, the elemental Hg will appear somewhere in the downstream processes. In cases where downstream equipment contains metals which amalgamate with Hg, the presence of liquid elemental Hg can cause Hg induced stress corrosion which could cause equipment failure.

We have found that the Hg concentration in liquid hydrocarbons, exemplified by a natural gas condensate containing about 120 $\mu\text{g/Kg}$, i.e., parts per billion (ppb) Hg, can be reduced to 10-20 ppb. This is accomplished by contacting the condensate with a carrier gas containing 200-500 parts per million of hydrogen sulfide. Typically, the gas containing hydrogen sulfide is mixed with the hydrocarbon containing elemental Hg and passed downflow over a packed bed. Typical reaction conditions are 150°C at a pressure of about 250 psia and a gas to liquid volumetric treating ratio of less than 2:1.

Because the amount of Hg in the condensate used was in the ppb range, it was not possible to recover any HgS for positive identification. However, it is believed that because the stainless steel filter used to filter the treated product acquired a red deposit, and since Cinnabar is the red HgS salt, it is reasonable to conclude that HgS is the product of the reaction.

INTRODUCTION

Some crude oils [1,2] and natural gas produced in various geographic locations [3,4] contain elemental Hg. In many of the gas producing fields, condensate is also produced in association with the gas. Typically if the gas produced contains Hg, the condensate recovered also contains Hg.

In the U. S., condensates are a valuable source of light distillates for the gasoline market [5]. About 500,000 bbl/day of condensate are used as refinery feedstock [6] and about 15,000 bbl/day in steam cracking for ethylene production [7]. In either application, the Hg in the condensate will have to appear somewhere in the downstream processes. Thus, it would seem that the fate of the Hg will be of concern. This is especially so in the case of steam cracking for ethylene production where equipment made of aluminum is used for cryogenic separation of the cracked products. Any elemental Hg contained in the cracked products is undesirable and could cause Hg induced stress corrosion. Similarly, stress corrosion could also be induced in other process equipment constructed of metals that have the ability to form amalgams.

To prevent Hg carryover and thus the potential corrosion of susceptible process equipment, it is desirable to remove elemental Hg from condensate. In this paper, we report the results of laboratory experiments using hydrogen sulfide as the agent for converting Hg^{2+} into HgS .

EXPERIMENTAL

- 1) Materials: a condensate containing about 120 $\mu g/Kg$, i.e., parts per billion (ppb) Hg. Nitrogen gas, methane gas, methane containing about 200 parts per million (ppm) hydrogen sulfide and carbon dioxide gas containing about 480 ppm hydrogen sulfide and about 2.5% methane.
- 2) Equipment: a down flow stainless steel reactor equipped with a mixing T, a preheat zone, temperature control, pressure control, a 1 ml section packed with 10-18 mesh Vycor chips, a 0.7 micron stainless steel product filter and appropriate liquid and gas flow controllers. Figure 1 is a schematic of the reactor and its ancillary systems.
- 3) Procedure:
 - a) Unit start up: from room temperature the gas flow and liquid flow were started and set at the required flow rates. The reactor was heated until the required temperature was reached. After about 10 minutes of steady operation, the product was collected periodically and sampled for Hg analysis.
 - b) Change of conditions: when changes in the process parameters or treating gas were made, the unit was not shut down. It was allowed to equilibrate at the desired conditions and after about 10 minutes of steady operation sampling/testing was resumed.
 - c) Hg determination: this was performed using the Jerome Hg Analyzer, Model 301.

RESULTS AND DISCUSSION

Hg reacts with H_2S to produce HgS and H_2 . Although the solubility of elemental Hg in various hydrocarbons [9] has been reported, that for HgS has not. However, the solubility of HgS in water is reported to be $2.8\text{E-}23$ g HgS /liter of water [10]. Since, in general, inorganic salts are more soluble in water than in hydrocarbons, it would be expected that HgS will be less soluble in the hydrocarbon condensate used than it is in water. Thus, the solubility of HgS in the treated condensate is expected to be less than $2.8\text{E-}23$ g HgS /Kg of condensate. Any HgS formed would not dissolve to any measurable extent in the treated condensate and possibly, could be removed from the treated product by filtration. Changes in the concentration of Hg in the concentrate will indicate its removal and thus the measure of the effectiveness of this approach is the reduction in the concentration of elemental Hg in the treated condensate.

In the reaction of Hg with H_2S , each mol of Hg requires 1 mol of H_2S . Since the concentration of Hg in the feed is about 120 ppb, the amount of H_2S required to react with it will be very small. Thus we decided to use carrier gases containing small amounts of H_2S in this study. The gases chosen were methane and carbon dioxide. Methane is the major component of natural gas and natural gas usually contains small amounts of H_2S . Also, in natural gas processing typically CO_2 and H_2S are removed from the gas before it can be marketed. In such removal processes, the treating solutions are regenerated and the gases leaving the regenerators contain CO_2 and H_2S . With this in mind methane/ H_2S and CO_2 / H_2S mixtures were selected for this study.

"Treating" with Carrier Gas

To determine if "treating" the condensate in the presence of a carrier gas changes the Hg concentration, experiments in which nitrogen and methane without H_2S were conducted at different temperatures and flow rates. In all cases no significant changes in the Hg content of the treated condensate were observed. From these observations it was concluded that heating the condensate in the presence of a carrier gas does not reduce the Hg content of liquid hydrocarbons.

Treating the Condensate with H_2S in Methane

Based on the concentrations of the 2 reactants, 200 ppm H_2S in methane, and 120 ppb Hg in the condensate, it can be shown that H_2S is in a large molar excess at any reasonable treating ratio. For example, when 1 volume of the treating gas is used to treat 1 volume of the condensate, the H_2S is in about a 20 molar excess.

- a) **Effect of Temperature** - At a gas to liquid treating ratio of 1:2.7, the treating efficiency increases as the treating temperature is raised. Table 1 shows our results. A plot of \ln of the concentration of Hg, in ppb, in the treated liquid after treatment vs $1/T$, in $^{\circ}\text{K}$, Fig. 2, gives the straight line:

$$\ln \text{ppb} = 1089 t + 0.95, \text{ where } t = 1/T.$$

- b) **Effect of Feed Ratio** - To study the effect of feed ratio on the efficiency of Hg removal, we varied the rate at which the condensate was pumped and kept the flow rate of the treating gas constant. At 150°C, the temperature chosen for this study, we found that at a treating ratio of about 1:1, the concentration of Hg in the treated condensate approaches about 10 ppb. The results of this study are shown in Table 2.

Treating the Condensate with H₂S in CO₂

Not unexpectedly, H₂S/CO₂ was also effective in reducing Hg from the condensate. Table 3 shows our results. At 150°C and a treating ratio of 1:1, the concentration of Hg in the treated condensate approached about 10 ppb.

This study was conducted at a constant temperature 150°C, and a constant gas flow rate, 23 ml/min, but at different condensate feed rates, 10-80 ml/min. Thus, from a plot of the reciprocal of the liquid hourly space velocity, LHSV, vs ln of the concentration of Hg, in ppb, in the treated condensate, Fig. 3, the rate equation, shown below, for the reaction between H₂S and Hg, can be derived.

$$\ln \text{ppb} = -78.4 v + 4.75, \text{ where } v = 1/\text{LHSV}$$

The slope of this equation gives the rate constant of the reaction in units of ln ppb Hg/hour.

Reaction Product

Because the amount of Hg in the condensate is in the ppb range, it was not possible to recover any HgS for positive identification. However, it is believed that because the stainless steel filter used to filter the treated product acquired a red deposit, and since Cinnabar is the red HgS salt, it is reasonable to conclude that HgS is the product of the reaction.

CONCLUSION

Laboratory results indicate that H₂S is an effective reagent for reducing the Hg content of hydrocarbon liquids. In this study, hydrocarbon liquids are exemplified by a condensate produced in association with natural gas and the H₂S is introduced in about 200-500 ppm in methane or carbon dioxide. At 150°C and about 180 seconds contact time, the Hg content of a condensate containing 120 ppb Hg can be reduced to about 10 ppb.

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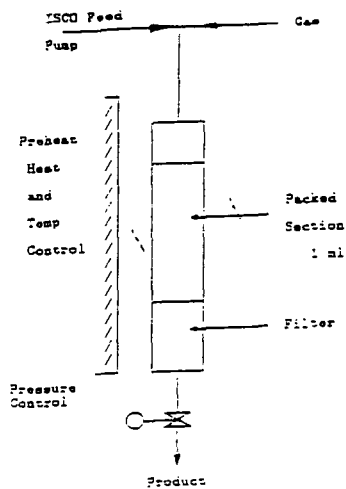


FIGURE 1
REACTOR FOR Hg REMOVAL

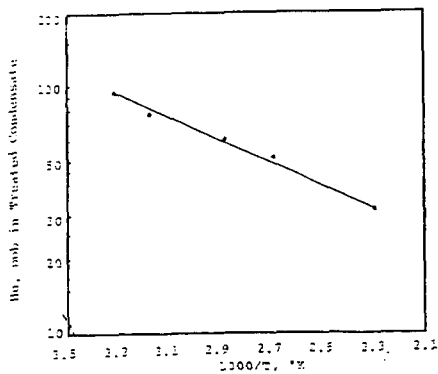


FIGURE 2
EFFECT ON FEED RATIO ON Hg REMOVAL

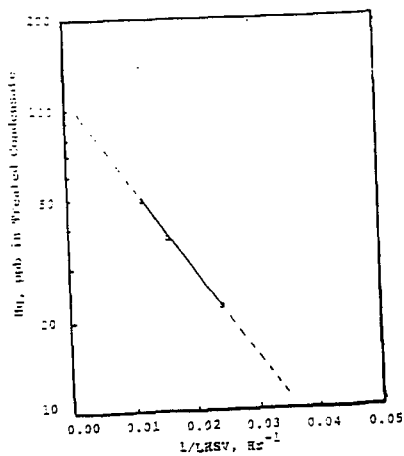


FIGURE 3
EFFECT ON FEED RATIO ON Hg REMOVAL

TABLE 1

Removal of Hg from Condensate (C) with H₂S in CH₄
Effect of Temperature

Gas: 200 ppm H₂S/balance CH₄
Packing: 1ml 10-18 mesh Vycor chips
Pressure: 220-260 psig

<u>Temperature</u> °C	<u>Volume ml/hr</u> <u>(C) CH₄/H₂S</u>		<u>Hg in Product</u> ppb	<u>Hg Removed</u> %
	Feed	----	116	----
29	70	26	95	19
43	70	26	77	34
75	70	26	60	49
100	70	26	52	55
165	70	26	31	74

TABLE 2

Removal of Hg from Condensate (C) with H₂S in CH₄
Effect of Feed Ratio

Gas: 200 ppm H₂S/Balance CH₄
Packing: 1 ml 10-18 mesh Vycor chips
Pressure: 220 - 260 psig
Temperature: 150 °C

<u>Volume ml/hr</u> <u>(C) CH₄/H₂S</u>		<u>Hg in Product</u> ppb	<u>Hg Removed</u> %
Feed	---	116	----
80	26	52	54
30	26	34	70
52	26	28	78
40	26	23,20,21	82
13	26	<10	>90

TABLE 3

Removal of Hg From Condensate (C) with H₂S in CO₂
Effect of Condensate to Gas Ratio

Gas: 500 ppm H₂S/2.5% CH₄/balance CO₂

Packing: 1 ml 10-18 mesh Vycor chips

Pressure: 220-260 psig

Temperature: 150 °C

<u>Volume, ml/hr</u> <u>(C) CO₂/H₂S</u>		<u>Hg in Product</u> <u>ppb</u>	<u>Hg Removed</u> <u>%</u>
Feed	----	116	----
80	23	50,47	58
60	23	38,36	68
40	23	17,21,19	84
20	23	<10,11,<10	>90
10	23	<10,<10,<10	>90